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ated ethylene-diphosphonium. I have identified these salts with those obtained by means of dichloride and dibromide of ethylene, both by a careful examination of their physical properties, and by the analysis of the characteristic iodide and of the platinum-salt. I have not been able to trace in the first of these reactions a salt of chlorethylated triethylphosphonium; but I have established by experiment that in the reaction between triethylphosphine and brominated bromide of ethyl, the formation of bromethyl-triethylphosphonium invariably precedes the production of the diphosphonium-compound.

XV. "Researches on the Phosphorus-Bases."—No. XI. Experiments in the Methyl- and in the Methylene-Series. By A. W. HOFMANN, LL.D., F.R.S. Received July 24, 1860.

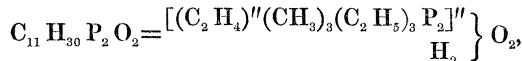
In former notes I have repeatedly called attention to the transformation of the bromide of bromethylated triethylphosphonium under the influence of bases. In continuing the study of these reactions, I was led to the discovery of a very large number of new compounds, the more important ones of which are briefly mentioned in this abstract.

HYBRIDS OF ETHYLENE-DIPHOSPHONIUM.

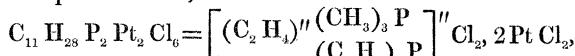
*Action of Trimethylphosphine upon Bromide of Bromethyl-triethylphosphonium.*

These two bodies act upon each other with the greatest energy, and moreover exactly in the manner indicated by theory. The resulting compound was of course examined only so far as was necessary to establish the character of the reaction.

The dibromide of the hybrid diphosphonium is more soluble than the hexethylated compound formerly described, which in other respects it resembles. Oxide of silver eliminates the extremely caustic base



which yields with hydrochloric acid and dichloride of platinum a pale-yellow platinum-salt,



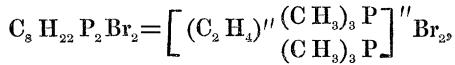
separating in scales from boiling water.

The salts of the hybrid diphosphonium crystallize like those of the hexethylated diphosphonium, but, so far as they have been examined, are somewhat more soluble. This remark applies especially to the iodide.

It seemed worth while to try whether the bromide of bromethylated triethylphosphonium was capable of fixing a molecule of phosphoretted hydrogen. It was found, however, that the two bodies do not act upon one another. Phosphoretted hydrogen gas, passed through the alcoholic solution of the bromide, either cold or boiling, did not seem to affect it in any way.

*Action of Trimethylphosphine on Dibromide of Ethylene.*

This reaction exhibits a repetition of all the phenomena observed in that which takes place between the dibromide and triethylphosphine. The process is completed sooner, if possible, than in the ethyl-series. The lower boiling-point and the overpowering odour of trimethylphosphine render it advisable to mix the materials with considerable quantities of alcohol or ether; and on account of the extreme oxidability of the phosphorus-compound, it is best to operate in vessels filled with carbonic acid and subsequently sealed before the blowpipe. After digestion for a short time at 100°, the mixture of the two liquids solidifies to a hard, dazzling, white, crystalline mass containing the two bromides,



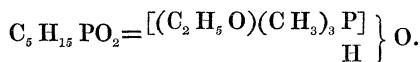
one or the other predominating according to the proportions in which the two bodies were allowed to act upon one another.

It was not difficult to establish the nature of these two compounds by numbers.

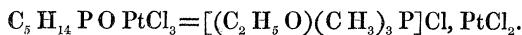
The solution of the saline mass in absolute alcohol, deposits, on cooling, beautiful prismatic crystals, consisting of the bromide of bromethyl-trimethylphosphonium almost chemically pure, while the diphosphonium-bromide remains in solution. The nature of the monophosphonium-compound was fixed by a bromine determination in the bromide, and by the analysis of a platinum-salt beautifully crystallized in needles containing



Treatment of this platinum-salt with sulphuretted hydrogen yielded an extremely soluble and deliquescent chloride, which was not analysed, but submitted to the action of oxide of silver, when it furnished the oxide of the corresponding oxethylated compound



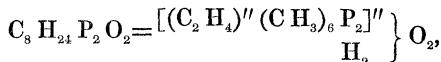
The caustic liquid was converted by hydrochloric acid into the easily soluble chloride corresponding to the oxide; and this chloride, when treated with dichloride of platinum, deposited the platinum-salt of the oxethylated trimethylphosphonium in well-formed octahedra extremely soluble in water, containing



*Salts of Hexmethylated Ethylene-diphosphonium.*

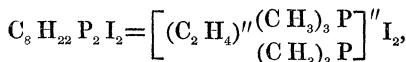
*Di-bromide.*—The preparation of this salt has already been mentioned. It is extremely soluble in water, and even in absolute alcohol, insoluble in ether. *In vacuo* over sulphuric acid it solidifies into a mass of acicular crystals, which are exceedingly deliquescent.

The dibromide, treated with oxide of silver, yields the corresponding dioxide,



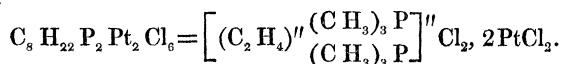
which forms with acids a series of salts resembling the corresponding ethyl-compounds. Of these I have prepared only the

*Di-iodide*, which crystallizes in difficultly soluble needles of the composition



surpassing in beauty the corresponding ethyl-compound, and the—

*Platinum-salt.*—This is an apparently amorphous precipitate, which is nearly insoluble in water, dissolves with extreme slowness in boiling hydrochloric acid, and separates therefrom on cooling in golden-yellow laminæ, very much like those of the platinum-salt of the hybrid ethylene-trimethyl-triethyl-diphosphonium. It consists of—

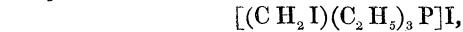


## METHYLENE GROUP.

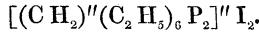
*Action of Triethylphosphine on Di-iodide of Methylen.*

Triethylphosphine and di-iodide of methylene act so powerfully on one another, that it is necessary to moderate the reaction by the presence of a considerable quantity of ether. The reaction is very soon completed, even when the mixture is largely diluted, especially if it be heated to 100° in sealed tubes. The saline residue left after the evaporation of the ether is immediately seen to be a mixture of several compounds, one of which—a sparingly soluble iodide crystallizing in long needles—at once arrests attention.

From analogy we might expect to find in the saline mixture the compounds



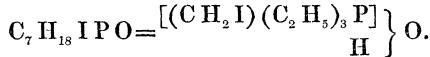
or



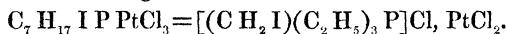
Experiment has, however, established the presence of the first only.

The difficultly soluble crystals just mentioned are easily purified, being readily soluble in water, sparingly in alcohol, insoluble in ether. Their solution in boiling alcohol yields splendid needles frequently an inch long, and possessing extraordinary lustre. Analysis prove this beautiful salt to be the first of the above-mentioned compounds.

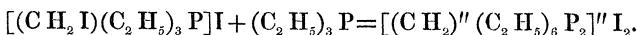
The new iodide behaves with nitrate of silver like the bromide of bromethylated triethylphosphonium; half the iodine is eliminated in the form of iodide of silver. It differs, however, from the bromide in its deportment with oxide of silver which, after removal of the accessible iodine, leaves the latent iodine untouched, even after protracted ebullition. A powerfully alkaline solution is thus obtained containing the base



The crystals of the iodide were transformed into the chloride by means of chloride of silver, and the solution was precipitated by dichloride of platinum. The precipitate is very sparingly soluble in cold water, but may be recrystallized from a considerable quantity of boiling water. As the liquid cools, splendid needle-shaped crystals are deposited containing



The sparingly soluble iodide is present in proportionally small quantity only among the products of the action of di-iodide of methylene on triethylphosphine. I have in vain endeavoured to detect among these products anything of the nature of a diphosphonium-compound. On treating the mother-liquor of the sparingly soluble iodide with chloride of silver, and the dilute filtered solution with dichloride of platinum, a few needles of the iodated platinum-salt are still deposited; but after considerable evaporation the solution yields crystals, all of which exhibit an octahedral habitus. I was equally unsuccessful in a particular experiment, in which I subjected di-iodide of methylene to the action of a large excess of triethylphosphine; and a similar report must be made of the attempt to produce the desired body by treating the ready prepared iodide with triethylphosphine, according to the equation



The examination of the mother-liquor of the sparingly soluble iodide is a difficult and thankless proceeding; nevertheless, by a sufficient number of iodine- and platinum-determinations, it may be shown to be a mixture of four different compounds. The mother-liquor is thus found to contain, together with the hydriodate of the phosphorus-base, two crystallizable iodides differing in solubility, and to be separated from one another only by a great number of crystallizations.

The more soluble salt is the iodide of oxymethylated triethylphosphonium, corresponding to the iodomethylated compound; the less soluble salt is the iodide of methyl-triethylphosphonium. The last mother-liquors contain considerable quantities of oxide of triethylphosphine.

*Iodide of Oxymethyl-triethylphosphonium.*

This salt is extremely soluble both in water and in alcohol, even in absolute alcohol, and crystallizes only after the alcohol has been completely evaporated. The crystals, resembling the frosty efflorescences on a window-pane, contain



The iodide, treated with oxide of silver, is converted into the corresponding caustic oxide, which, when mixed with hydrochloric acid and dichloride of platinum, yields a rather easily soluble platinum-salt of an octahedral habitus.

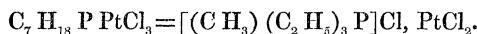
*Iodide of Methyl-triethylphosphonium.*

The nature of the less soluble iodide was determined by an iodine-determination, and by the analysis of the platinum-salt. The iodide dissolves in water and in alcohol, but is insoluble in ether. By adding ether to the alcoholic solution, tolerable crystals are obtained. This compound is most conveniently purified by precipitating the alcoholic mother-liquor, after freeing it by crystallization as far as possible from the iodomethylated iodide, with a quantity of ether insufficient to precipitate the whole, so that the greater part of the iodides may remain in solution.

The iodide thus prepared contains



For further verification of this formula the crystals were deiodized with silver-oxide, and the caustic liquid thus obtained was saturated with hydrochloric acid and precipitated by dichloride of platinum. The platinum-salt, which crystallizes in beautiful octahedra, was found to contain



The two iodides are accompanied by a considerable quantity of oxide of triethylphosphine, which immediately separates in oily drops on treating the last mother-liquor with potash. Its presence was likewise unmistakeably recognized by the preparation of the platinum-salt. If the last mother-liquor of the iodine-compounds be deiodized and mixed with hydrochloric acid and dichloride of platinum, a quantity of octahedral salts separates in the first place, which are removed by sufficient concentration; the remaining liquid, when mixed with alcohol and ether, yields a crystalline precipitate, which separates from alcohol by spontaneous evaporation in the beautiful large hexagonal tables consisting of the platinum-salt of the oxychloride of triethylphosphine, which has been more fully described in one of the previous notes on these researches.

The formation of the four compounds contained in the mother-liquor of the sparingly soluble iodide is illustrated by the following equations:—

